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Two-dimensional correlation ATR-FTIR studies on PEO–PPO–PEO tri-block copolymer and its phosphorylcholine derivate as thermal sensitive hydrogel systems

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ABSTRACT

In this work, both 1D and 2D ATR-FTIR analyses were applied to study the behaviors of the PEO–PPO–PEO tri-block copolymer (Pluronic-F88) aqueous solution during the thermal gelling process. Furthermore, a novelly synthesized phosphorylcholine-modified F88 was also studied by the same technique, for the explanation to its different performance in the rheological study, as compared to F88. It was mainly focused on the changes in the water structure between sol and gel states, and the interactions between chemical bonds in the polymer chains with water molecules at a molecular level.

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1. Introduction

"Smart" hydrogels which are sensitive to the temperature, ionic strength or pH value [1–7] have been extensively studied for their potential applications in site-specific controlled drug delivery and bio-separation [8–10]. Among these, the commercialized PEO–PPO–PEO tri-block copolymer named Pluronic or Poloxamer was already applied in some cases [11,12] for its well studied thermal reversible gelation properties.

The PEO–PPO–PEO block copolymers can be dissolved in water in the form of unimer at low temperature. With the increase of concentration or temperature, critical micellization concentration or critical micellization temperature of its aqueous solution can be observed, while the aggregation of PEO–PPO–PEO block copolymers occurs with the micellization followed by a close packing process [13–18]. Though the general micellization and gelation behavior of PEO–PPO–PEO block copolymers have been extensively studied, the "molecular level" mechanism of micellization and gelation remains a controversial issue [1].

Mechanism studies on the characterization and sol–gel phase transitions of Pluronics using various instrumental techniques [13,18,19]. Among those, Liu et al. have achieved great success in studying the effect of temperature, concentration, ionic strength, etc. on the phase transition of Pluronic hydrogels using ATR-FTIR [20–25]. Also FTIR was employed in studying other thermal sensitive hydrogel systems [26].

Recently, two-dimensional (2D) correlated ATR-FTIR technique, which had been reported to be useful in investigating the dynamic variations, was employed in addition to the normal 1D ATR-FTIR studies. The generalized 2D correlation spectroscopy proposed by Noda [27–29], which is an extension of the original 2D correlation spectroscopy, has recently been proved as a powerful tool in studying the molecule–molecule interactions in some particular systems [30–32]. In this kind of 2D analysis, two kinds of correlation maps, synchronous and asynchronous, are generated based upon a set of dynamic spectra calculated from the fluctuations of the spectroscopic signals during the process under examination. The generalized 2D method can handle signal fluctuating as an arbitrary function of time or any other physical variables such as temperature, pressure, or concentration [29,33–36].

In the present study, Pluronic F88 modified with the phosphorylcholine (PC) moieties was synthesized, which had the "bio-inspired" structure of the membranes of the erythrocyte cells. Such modification was reported to be able to considerably improve the anti-thrombus properties and anti-protein adhesion of biomedical polymers [37,38] as well as introduce some special interactions between the polymer chains [39,40]. The thermally induced gelation process of the aqueous solutions of F88 and phosphorylcholine end-capped F88 (PC88), including the water structure changes between sol and gel states, and the interactions between chemical bonds in the polymer chains with water molecules were analyzed

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by 2D ATR-FTIR technique at a molecular level. A preliminary rheological study was also performed in the present work for the further investigation of the difference between PC88 and F88 in their gelation behaviors.

2. Experiments

2.1. Materials

The PEO–PPO–PEO tri-block copolymers were purchased from BASF. In the present study, Pluronic® F88 with the structure of $EO_{97}PO_{39}EO_{97}$ was used. 2-Chloro-2-oxo-1,3,2-dioxaphospholane (COP) was synthesized in our lab as previously reported [38], which was characterized using the GC–MS technique (Voyager), with the purity of 97%. All the other raw materials and solvents were dried and purified according to standard methods.

2.2. Synthesis of phosphorylcholine-modified F88

The phosphorylcholine end-capped F88 denominated as PC88 was prepared by the similar method we have used for the preparation of phosphorylcholine-modified poly-ε-caprolactone and chitosan in our previous reports [38]. The synthesis process was described briefly as follows.

Pluronic® of 0.01 mol either F88 or together with 0.02 mol triethylamine (TEA) was dissolved in 100 mL dried THF in a flask purged with nitrogen. The solution of 0.02 mol COP and 50 mL THF was added on gentle agitation within 3 h through a pre-dried dropping funnel. All operations were performed at 0 °C. Then the system was slowly warmed to room temperature and stirred for another 2 h before removing the solvent from the intermediate COP–Pluronic on a rotary evaporator under reduced pressure. Then COP–Pluronic was moved to another round-bottom flask and 40 mL dry acetonitrile saturated with trimethylamine (TMA) was added. The solution was heated at 65 °C and then maintained on gentle agitation for 48 h. Residual TMA was removed on careful heating and then precipitated in cold petroleum ether. The precipitate of phosphorylcholine end-capped Pluronic was collected and after subsequent dissolution/precipitation cycle with THF/petroleum ether, it was dried *in vacuo* to constant weight.

F88 and PC88 were resolved in distilled water at a concentration of 20 wt%, respectively, and restored at 4 °C for 3 days before the measurement to have a more sufficient dissolution.

2.3. ^{1}H NMR study

^{1}H NMR spectra of F108, F127, PC108 and PC127 were recorded in $CDCl_3$ with a Bruker model AVANCE DMX-500 spectrometer using tetramethylsilane (TMS) as an internal standard.

2.4. ATR-FTIR characterization

The 20% aqueous solutions of F88 and PC88, respectively, were cast into an ATR cell with a ZnSe reflection element, which was attached to a Nicolet Nexus Smart ARK FTIR spectrometer equipped with a DTGS detector. About 4 mL of the polymer solutions was used to fill the ATR cell and covered with a plastic plate during the measurement for the limitation of the water evaporation. The temperature-resolved ATR-FTIR test began at 25 °C, when the polymer solutions appeared in a sol state. The spectrum of the solution at this temperature was collected at a spectral resolution of 4 cm^{-1} by accumulating 128 scans. Then the temperature of the ATR cell was raised by 1 °C and equalized for 10 min before another spectrum was collected with the same parameters. This process was repeated until the cell temperature reached 45 °C when the polymer solutions had already undergone a complete sol–gel transition to the state of hydrogels. Thus, there were totally 21 spectra collected for F88 and PC88. The measurements were carried out within the wavenumber range of 4000–650 cm^{-1}. All of the original spectra were smoothed and baseline corrected using Omnic 6.0 software.

2.5. 2D-IR calculation

For the generalized 2D correlation analysis, in both the system of F88 and PC88, all the 21 spectra collected at every temperature point were selected and subjected to the 2D software named 2D Pocha (developed by Daisuke Adachi, Kwansei Gakuin University, Nishinomiya, Japan). Three domains in the spectra located at 1800–1500, 1400–1300 and 1200–1000 cm^{-1}, respectively, were focused for the information of the variations occurred in the systems throughout the thermal sensitive gelation process at a molecular level.

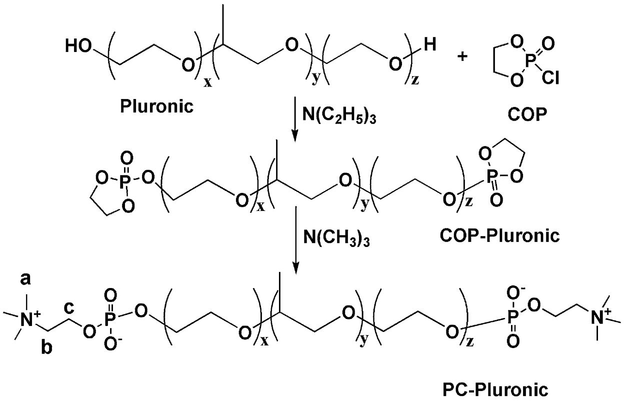
2.6. Rheological study

Storage (G') and loss (G'') moduli of F88 and PC88 hydrogels were recorded by the Advanced Rheometric Expansion System (ARES, Rheometric Scientific), equipped with a Couette geometry accessory. All the samples were dissolved in distilled water to make 20 wt%, solutions of which were stored at 4 °C for 3 days before the measurement. During a dynamic temperature scanning rheological study, the sample solution was poured into the Couette geometry accessory and was carefully overlaid with a lower density 50 CP silicone oil to minimize drying and evaporation. The measurements were conducted on shear modulus as a function of temperature. A frequency of 10 rad/s was employed. The heating rate was 0.5 °C/min from 10 to 60 °C. The strain amplitude for all the measurements was set at 10% in the linear range where moduli were almost independent of strain amplitude.

3. Results and discussion

3.1. Structural characterization of F88 and PC88

Changes in the terminal groups of the PEO–PPO–PEO tri-block copolymers could be observed in ^{1}H NMR spectra. The terminating hydroxyl group in original F88 tri-block copolymer (Scheme 1) provided chemical shift at 2.51 ppm. In the spectra of PC 88 (Fig. 1), the peak of the hydroxyl group almost totally disappeared, while at the same time three new peaks appeared. They were located at 2.57 (peak a), 3.09 (peak b) and 4.25 ppm (peak c), respectively (consult Scheme 1 and Fig. 1). These groups of peaks corresponded to the protons of the PC groups (Scheme 1).



Scheme 1. Chemical structures of F88 and PC88.

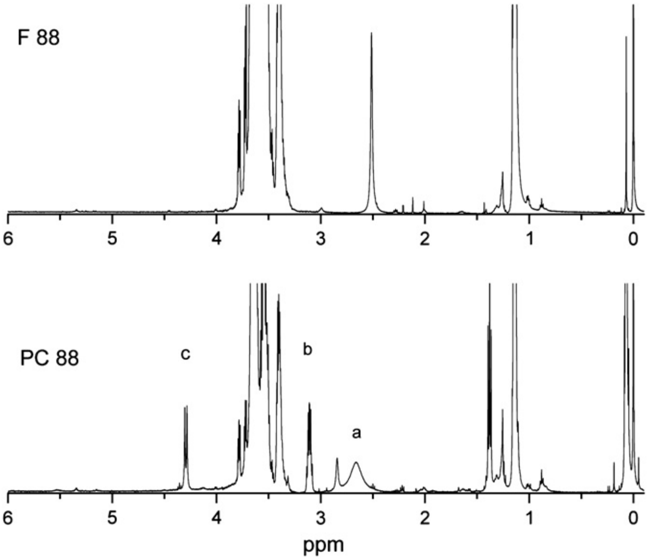


Fig. 1. ^{1}H NMR spectra of F88 and PC88 in $CDCl_3$.

3.2. Investigation of waters in the hydrogel systems during transition

The IR spectra, especially the 2D spectra, have already been proved to be powerful tools in the investigation of the water structures inside polymeric materials [41]. In the present study, changes in the spectra of F88 and PC88 in the range of 1800–1600 cm^{-1} were investigated to study the water structure changes in these two hydrogel systems during their sol–gel transitions.

As shown in Fig. 2a and b, the FTIR spectra of aqueous solutions F88 and PC88 showed no significant differences through their gelation process with the change of the temperature. There was an increase in 1637 cm^{-1} with the temperature rising, while this peak was narrowed with the shoulder located at around 1690 cm^{-1} disappeared. The former peak was attributed as the δ(OH) band of free water in the system, while the latter was assigned to the δ(OH) band of hydrogen bonded water (bound water). Compared with the peak position of the free water, the bending vibration band of water would shift to the higher wavenumber after the formation of the hydrogen bonds [42]. These results indicated that in the system of both F88 and PC88, a transition from bound water to free water happens during the thermal induced gelation process [21,22].

It could be observed that the only difference between the two groups of the spectra in Fig. 2 was that the spectra of F88 had a milder temperature than that of PC88. This was supposed to be the result of the not so completed sol–gel transition of the PC88 hydrogel compared to the F88 induced by the ultra-hydrophilic phosphorylcholine end groups.

In the 2D correlated ATR-FTIR spectra, the PC88 system also performed a very similar result with the F88 system in the spectral region of 1800–1500 cm^{-1}. The 2D-IR spectra of F88 within 1800–1500 cm^{-1} are illustrated in Fig. 3, where panel a shows the synchronous correlation spectrum and panel b shows the asynchronous correlation spectrum. In the synchronous contour map, one auto peak located at 1637 cm^{-1} could be obviously observed; as described above, this auto peak is assigned to the δ(OH) band of free water, the high intensity of this peak shows the change of the relatively high content of the free water during heating. One negative cross-peak at 1637/1690 cm^{-1} could also be found, and the band at 1690 cm^{-1} is attributed to the δ(OH) band of bound water. This negative cross-peak indicated that the two peaks at 1690 and 1637 cm^{-1} varied contrarily, which could help to conclude that there existed the transition between bound water and free water during the whole gelation process, in accordance with the 1D-IR results mentioned above.

More information could be derived from the corresponding asynchronous correlation spectrum in Fig. 3b. The asynchronous correlation spectrum is anti-symmetric with respect to the diagonal line. In the 2D spectrum, an asynchronous cross-peak appears only if the intensities of two spectral features change out of phase (*i.e.*, delayed or accelerated) with each other. Thus, the absence of an asynchronous cross-peak denotes that the two spectral features change synchronously [27,28]. Two negative cross-peaks (1641/1637, 1690/1637 cm^{-1}) and one positive cross-peak (1637/1585 cm^{-1}) could be observed in Fig. 3b, indicating that the broad δ(OH) water band in the region of 1800–1500 cm^{-1} was split to three separate bands locating at 1690, 1641, 1637 cm^{-1}, respectively.

The sign of the cross-peaks in an asynchronous spectrum would provide additional information about the order of the intensity changes in different bands. According to the rule of Noda [27,28], and the positive sign of the cross-peak at 1641/1637 cm^{-1} in the slice spectrum, the band at 1690 cm^{-1} varied prior to the two bands at 1637 and 1641 cm^{-1}, respectively, while the band at 1641 cm^{-1} changed even after the band at 1637 cm^{-1} (1690 cm^{-1} $>$ 1637 cm^{-1} $>$ 1641 cm^{-1}). Thus, the signs of the 2D-IR asynchronous spectrum suggested that there occurred a transition from bound water centered at 1690 cm^{-1} to free water at around 1640 cm^{-1} (1637 and 1641 cm^{-1}). Furthermore, the bound water varied prior to the free water. It was previously reported that the Pluronic molecules, especially the PPO segments in this kind of thermal sensitive hydrogel undergo a dehydration process when heated to a certain critical temperature to form hydrophobic cored micelles, followed by the sol–gel transition due to the close packing of these spherical micelles [21,22,24,25]. This dehydration process would also, as a result, free most part of the bound water which are

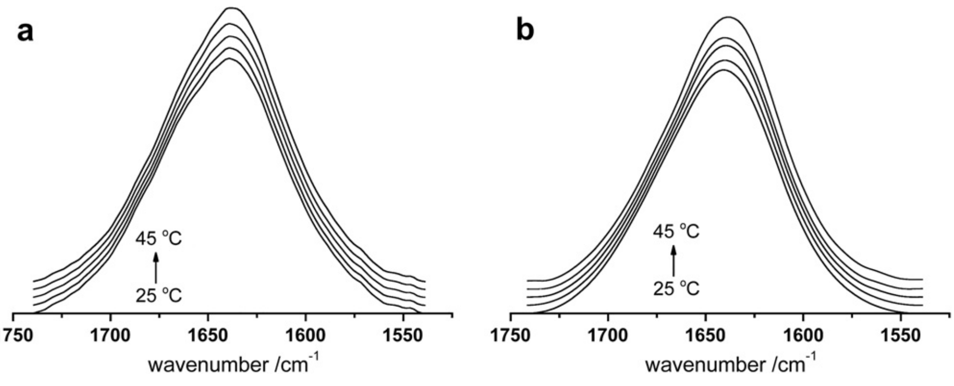


Fig. 2. 1D ATR-FTIR spectra of F88 (a) and PC88 (b) in the region 1800–1500 cm^{-1} corresponding to temperature variation from 25 to 45 °C.

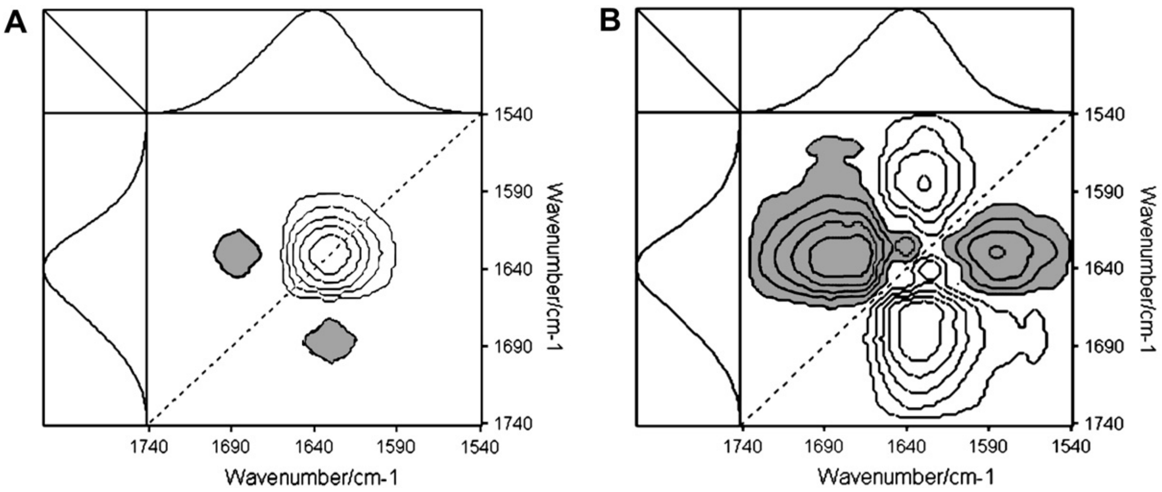


Fig. 3. 2D correlated ATR-FTIR spectra of F88 in the 1800–1500 cm^{-1} wavenumber region: (A) synchronous; (B) asynchronous contour maps. (In 2D-IR correlation spectra, the unshaded and shaded areas in the contour maps represent positive and negative peaks, respectively, and the averaged 1D reference spectrum is represented at the left side and at the top of the map.)

hydrogen bonded to the polymer chains. In the present study, the change from bound water to free water was investigated, providing the evidence of the dehydration process. Furthermore the variation sequence of the water structure in the system was also confirmed by 2D-IR study.

3.3. *Study on the methyl and methylene groups in the gelation process*

For a further study of the dehydration process, the IR spectra in the region of 1400–1300 cm^{-1} of both F88 and PC88 were investigated in corresponding to the temperature variation (Fig. 4). This region was reported to offer the information about the symmetric deformation vibration of methyl groups and CH_2 groups [43,44]. It could be observed that variations of three bands were involved in this region, locating at 1381, 1373 and 1350 cm^{-1}, respectively. In both the groups of IR spectra of F88 and PC88, band at 1381 cm^{-1} performed a red shift to 1373 cm^{-1}, while the band at 1350 cm^{-1} kept decreasing during the heating process. The first two bands were assigned to the symmetric deformation vibration of methyl groups in the PPO segments as reported [21,22] in which the band at 1381 cm^{-1} was assigned to the hydrated state of the methyl groups surrounded by water and the band at 1373 cm^{-1} was assigned to the dehydrated state. The assignment of the band at 1349 cm^{-1} had also been reported as the amorphous phase of PEO segments [21,22]. Thus, the following conclusion can be drawn from the temperature-resolved 1D ATR-FTIR spectra of the 20 wt% aqueous solutions of F88 and PC88 in the domain 1400–1300 cm^{-1} as shown in Fig. 4a and b: the methyl groups in the PPO segments undergo a dehydration process with the temperature increasing, corresponding to the band at 1381 cm^{-1} shifted to 1373 cm^{-1} when heated; and there was a transition of the PEO segments from amorphous phase to the crystalline phase during the gelation process.

With the powerful tools of the 2D correlated spectra, the dehydration behaviors could be further analyzed. Also the PC88 system performed very similar to F88 in 1400–1300 cm^{-1} in the 2D-IR analysis. The 2D-IR spectra of F88 within 1400–1300 cm^{-1} are shown in Fig. 5, in which panel a shows the synchronous correlation spectrum and panel b shows the asynchronous correlation spectrum. In the synchronous spectrum, three auto peaks could be found at 1383, 1370 and 1350 cm^{-1}, respectively, indicating that these three bands varied during the thermal induced gelation process of the F88 solution. The assignment of the bands had been described in the temperature dependent 1D-IR spectra already [24,25]. Two negative cross-peaks at 1383/1370 and 1371/1350 cm^{-1}, respectively, and one positive cross-peak at 1383/1350 cm^{-1} were also observed in the synchronous map. These cross-peaks offered the information about the change directions of the bands involved during heating that the bands at 1383 and 1350 cm^{-1} changed in the same direction, while the band at 1370 cm^{-1} changed contrarily. Further information was provided with the cross-peaks in the asynchronous 2D-IR contour map. Two main cross-peaks at 1383/1350 cm^{-1} and at 1370/1350 cm^{-1}, positive and negative, respectively, could be found in the asynchronous spectrum, with another positive "shoulder" at 1383/1370 cm^{-1}. The variation

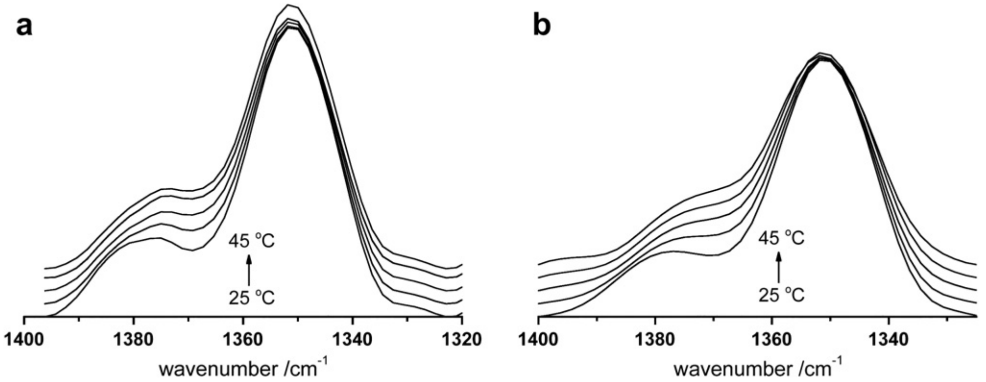


Fig. 4. 1D ATR-FTIR spectra of F88 (a) and PC88 (b) in the region 1400–1300 cm^{-1} corresponding to temperature variation from 25 to 45 °C.

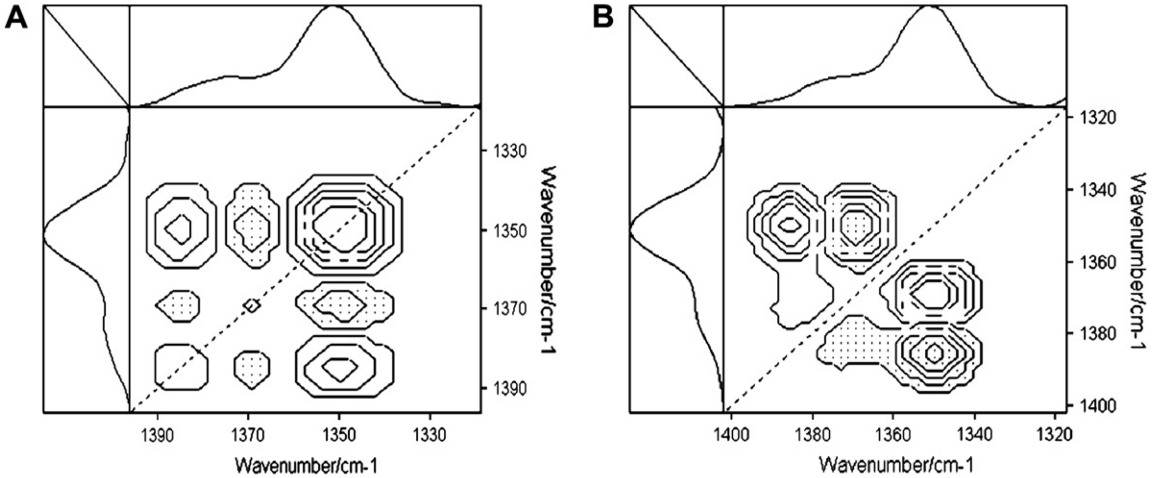


Fig. 5. 2D correlated ATR-FTIR spectra of F88 in the 1400–1300 cm^{-1} region: (A) synchronous; (B) asynchronous contour maps.

sequence of the bands involved could be thus confirmed in the light of Noda's rules [27,28]. The band at 1350 cm^{-1} varied after both the bands at 1370 and 1383 cm^{-1}, while the band at 1370 cm^{-1} changed prior to the band at 1383 cm^{-1}, *i.e.*, 1370 → 1383 → 1350 cm^{-1}. The dehydration process could be proved here again for the sequenced change between the bands represented the hydrated methyl groups and the dehydrated methyl groups. Furthermore, the change of the band at 1350 cm^{-1} assigned to the CH_2 wagging vibration of the amorphous state, occurred after the changes of the bands related to the dehydration process, indicating that the transition of the PEO segments to the crystalline phase was partly induced by the dehydration process of the PPO segment during the thermal sensitive sol–gel transition of the Pluronic aqueous solution.

3.4. *Study on the ether groups during the sol–gel transition*

Spectral changes occurred in the domain of 1200–1000 cm^{-1} were investigated to study the variations of the C–O–C bonds during gelation, because there was a strong band at around 1080 cm^{-1} assigned to the conjugation of the C–O–C stretching vibration of both PPO and PEO blocks [43,44]. It was reported that there was also a dehydration process of the ether backbone with the temperature increasing, causing a band shift to the higher wavenumber and band width broadening because of the disorder of the conformation of the C–O–C skeletons with the different dehydration degrees of PPO and PEO segments [21]. In the present study, in the temperature-resolved 1D ATR-FTIR spectral series, F88 performed such a behavior as reported: the band at 1085 cm^{-1} decreased when heated while the band at around 1120 cm^{-1} kept increasing; the band width broadening of 1085 cm^{-1} was also observed. The band at around 1120 cm^{-1} was thus assigned to the dehydrated C–O–C bonds as the C–O–C bands were at higher wavenumbers when Pluronic was in solid state [21]. However, PC88 didn't show such a clear dehydration process as F88 in its FTIR spectra, probably because of the hindrance from its hydrophilic end groups, though there was still a decrease of the band at 1085 cm^{-1} with the temperature increasing (Fig. 6).

In the 2D-IR analysis of the temperature-resolved spectra in the region 1200–1000 cm^{-1}, F88 and PC88 appeared to be different in the synchronous and asynchronous contour maps. In the case of F88 as shown in Fig. 7A and B, one broad auto peak at about 1120 cm^{-1} could be observed in the synchronous spectrum, with a negative cross-peak located at 1120/1085 cm^{-1} in the asynchronous contour map. Therefore, it could be concluded that bands at 1120 and 1085 cm^{-1}, which had already been assigned to the band of dehydrated ether bonds and hydrated ether bonds, respectively [24,25], were involved and correlated in the whole process. The shape of the negative cross-peak in the asynchronous contour maps indicated that this cross-peak was formed in the correlation of the variation of a broad band at around 1120 cm^{-1} with the variation of the band at 1085 cm^{-1}. As described in the 1D FTIR spectral study, the dehydrated C–O–C bands would split because of the different dehydration degrees between PPO and PEO segments. Furthermore, the 2D-IR analysis could also tell us that the band at 1085 cm^{-1} varied earlier than the band at around 1120 cm^{-1}.

In the 2D correlated ATR-FTIR contour maps of PC88 of 1200–1000 cm^{-1} wavenumber region as shown in Fig. 8, which were much different from those of F88, two auto peaks at 1120 and 1085 cm^{-1} could be found in the synchronous spectrum, with a negative cross-peak at 1120/1085 cm^{-1}; and in the asynchronous

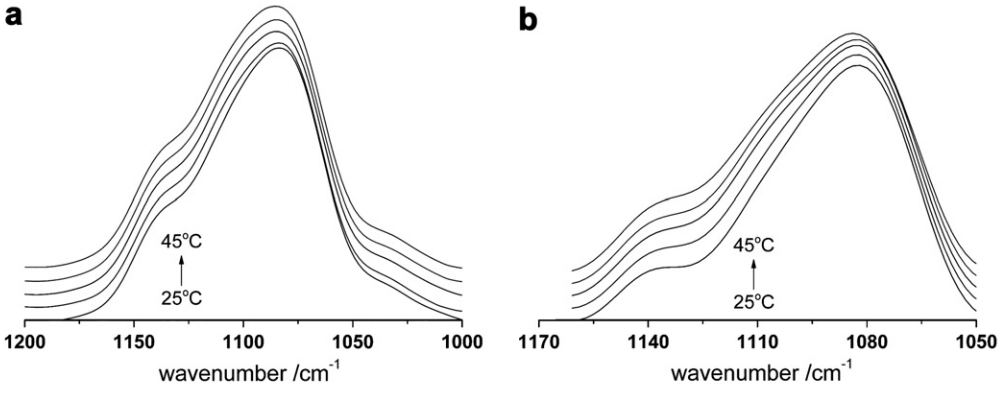


Fig. 6. 1D ATR-FTIR spectra of F88 (a) and PC88 (b) in the region 1200–1000 cm^{-1} corresponding to temperature variation from 25 to 45 °C.

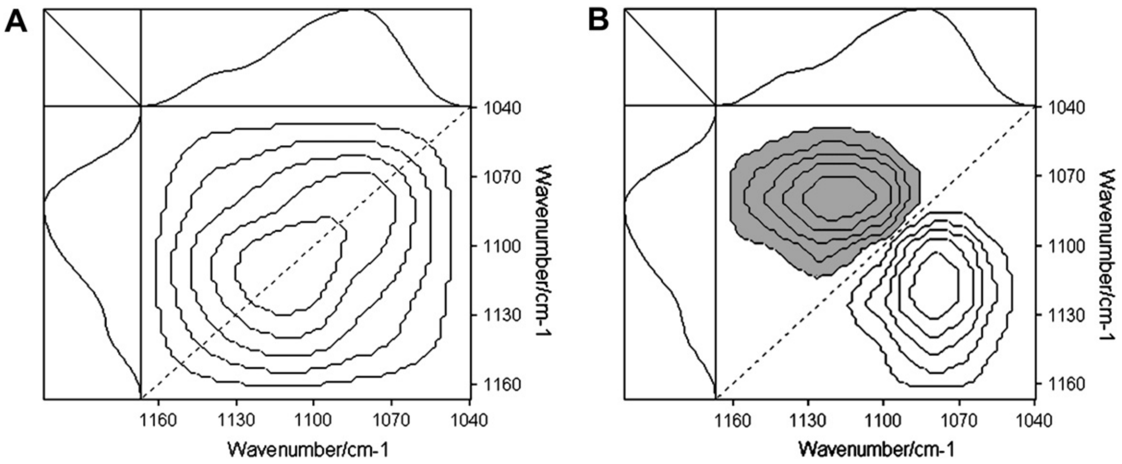


Fig. 7. 2D correlated ATR-FTIR spectra of F88 of 1200–1000 cm^{-1} wavenumber region: (A) synchronous; (B) asynchronous contour maps.

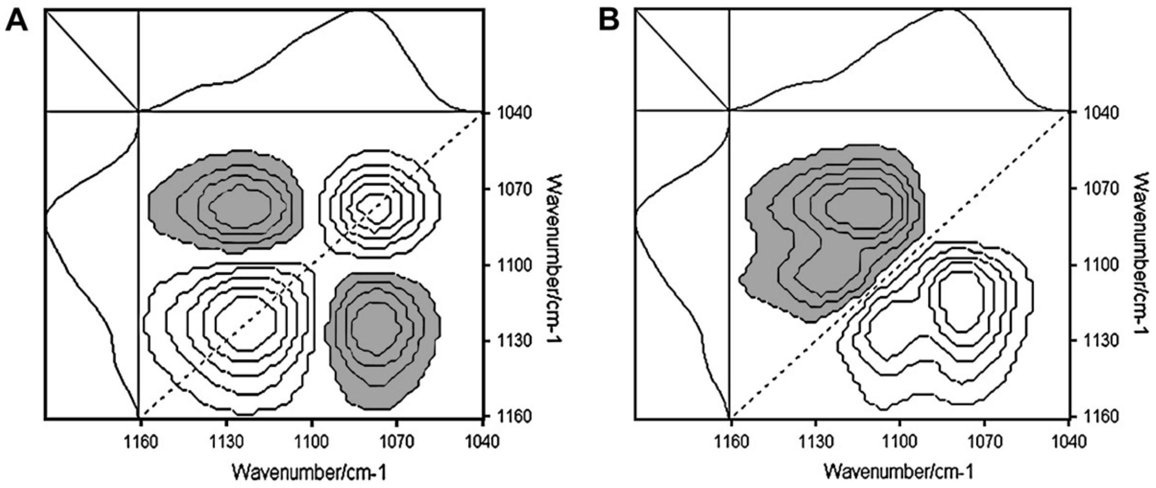


Fig. 8. 2D correlated ATR-FTIR spectra of PC88 of 1200–1000 cm^{-1} wavenumber region: (A) synchronous; (B) asynchronous contour maps.

spectrum, one strong negative peak at 1120/1085 cm^{-1} can be observed with a relatively weak cross-peak at 1120/1100 cm^{-1}. The relationship between the band at 1120 and 1085 cm^{-1} had already been discussed above in the case of F88. Similarly, the PC88 hydrogel also showed a dehydration process of the C–O–C bonds, with the band at 1200 cm^{-1} changed earlier than that at 1085 cm^{-1} in this system.

The additional band at 1100 cm^{-1} was contributed to the P–O–C bonds in the phosphorylcholine end groups (always having the IR band at 1070 cm^{-1} in the solid state [45], which was hard to be recognized in 1D-IR of PC88 because of the overlapping with the band of C–O–C bonds) involved in the gelation process. The correlations and relationships of this band with other bands were not clear in the 2D maps because of the relatively low content of the PC end groups in the system.

It was suggested that the PC groups were involved in the dehydration of the C–O–C bands, which finally affected the gelation behaviors as we have discussed before, by affecting the micellization and close packing process during the sol–gel transition. In order to further prove this hypothesis, the thermally induced sol–gel transition behaviors of the 20 wt%, solutions of F88 and PC88 were compared by rheological measurements and the results are shown in Fig. 9. It was found that the original solution of F88 at the concentration of 20 wt% began to gelatinize at about 39 °C, and the gelation process was fast, with the storage modulus increasing from about 0 to 1000 Pa. However, in the case of the PC88 solution at the same concentration, although it also had a gel transition, the transition onset shifted to 42 °C, with the storage modulus increasing from about 0 to only 600 Pa. The strength of the PC88 hydrogel was lower and the gelation process was slower compared to the unmodified F88 hydrogel.

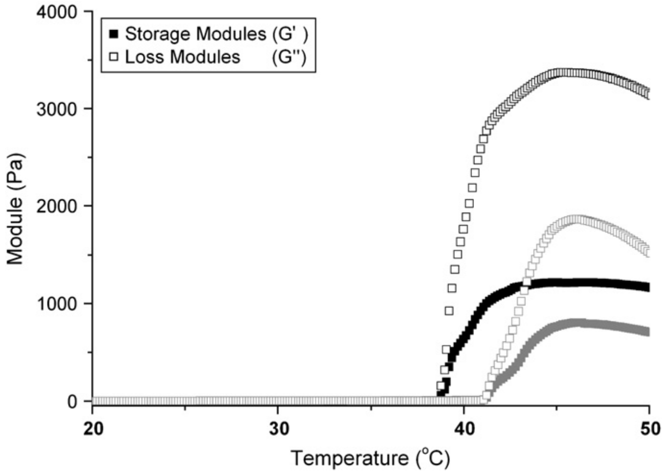


Fig. 9. Dynamic rheological temperature scan at the heating rate of 0.5 K/min of F88 (20 wt%, black) and PC88 (20 wt%, grey) solutions, stain = 10%, frequency = 10 rad/s.

Thus, it could be concluded that the super hydrophilic PC groups attached to the PEO–PPO–PEO molecules might have interfered with their dehydration process with huge amounts of water remaining in the micelles and this might lead to the inadequately micellization of the molecules. This would certainly affect the formation of the physically crosslinking structures induced by the close packing of the micelles, which macroscopically resulted in a relatively low hydrogel strength and slower gelation speed.

4. Conclusions

In the present article, 1D and 2D ATR-FTIR of F88 and PC88 aqueous solutions were carefully studied and compared for the investigation of the changes in water structure, polymer chain conformation and polymer–water interactions occurred in the thermally induced sol–gel transition of these hydrogels. A dehydration process was observed in both F88 and PC88 systems with the gelation process happened, with the variation of the chemical bonds involved sequenced by 2D analysis. And the crystalline process of PEO segments was confirmed to be related with the dehydration of the methyl groups. Furthermore, there was an evidence that the phosphorylcholine end groups of PC88 involved in the dehydration process that made difference between its gelation behaviors from F88 in their aqueous solutions, which was further confirmed by rheological measurements.

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